

Submitted to:

National Aeronautics and Space Administration
Marshall Space Flight Center
MSFC, AL 35812

IN-07-10
152469
P.21

Attention: Contracting Officer's Technical Representative, K. Y. Ogle (1 copy)
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TR-1619-1-1

TECHNICAL PROGRESS REPORT

Integrated Oxygen Recovery System

Technical Progress Report No. 1

Prepared Under

Program No. 1650

for

Contract NAS8-39843

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March 8, 1993

N93-22663

Unclas

G3/54 0150469

(NASA-CR-192343) INTEGRATED OXYGEN
RECOVERY SYSTEM bimonthly Technical
Progress Report No. 1, 8 Jan. - 8
Mar. 1993 (Life Systems) 21 p

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LIST OF ACRONYMS

GC	Gas Chromatograph
ORS	Integrated Oxygen Recovery System
PEEK	Polyetheretherketone
SBIR	Small Business Innovation Research
SMC	Solid Metal Cathode

1.0 WORK PERFORMED DURING REPORTING PERIOD

This Technical Progress Report summarizes the work performed from the start of Contract No. NAS8-39843 (01/08/93) through 03/08/93. This contract is a Phase I Small Business Innovation Research (SBIR) program to demonstrate the feasibility of the Integrated Oxygen Recovery System (IORS). The IORS is applicable to advanced mission air revitalization. It provides the capability for electrochemically generating metabolic oxygen (O_2) and recovering O_2 from the space habitat atmosphere via a carbon dioxide (CO_2) reduction process within a single assembly. To achieve this capability, the IORS utilizes a novel Solid Metal Cathode (SMC) water electrolysis unit that simultaneously serves as the Sabatier CO_2 reduction reactor.

The IORS would enable two major life support systems currently baselined in closed loop air revitalization systems to be combined into one smaller, less complex system. It would reduce fluidic and electrical interface requirements and eliminate a hydrogen (H_2) interface. Furthermore, since the IORS utilizes an SMC, the system has the additional capability to generate high pressure O_2 (i.e., $\approx 1,000$ psia) for recharging extravehicular activity O_2 bottles. This capability is not part of currently baselined or planned technologies.

During this Phase I SBIR program we will evaluate the IORS process by demonstrating its performance and quantifying key system physical characteristics, including power, weight and volume.

Work performed during this reporting period included preliminary modeling of the electrolysis and methanation functions within the IORS, and the design and fabrication of a Breadboard IORS and its test setup.

1.1 Mathematical Modeling

Task 1.0 of the program involves the development of the preliminary mathematical models to predict the performance of the SMC electrolyzer and the performance of the Sabatier reaction in the IORS configuration. These preliminary models will be revised later, based on testing of the Breadboard IORS.

1.1.1 SMC Electrolyzer Model

This section presents the mathematical model of the water electrolysis function of the IORS. A model for the transport of H_2 through a SMC was developed under Contract No. NAS2-11829.^(a) This model has been updated during the current program in order to convert from English to SI units.

(a) Grigger, D. J. and Schubert, F. H., "Static Feed Water Electrolysis Subsystem Development," Final Report, Volume II, TR-603-25-2, Contract NAS2-11829; Life Systems, Inc., Cleveland, OH; December, 1988.

The reactions occurring in the SMC water electrolysis cell are shown in Figure 1-1. Water is reduced at the cathode, forming hydrogen atoms (H) which diffuse through the SMC because of a difference in the partial pressure of H₂. On the side of the SMC at which a lower partial pressure for H₂ exists, two hydrogen atoms combine to form H₂. In the cell shown in Figure 1-1, the H diffuses into the interior of the SMC tube.

The efficiency for the transmission of H₂ through the SMC is given by the expression shown in Table 1-1. This expression was developed from experimental data using a multiple linear regression routine. The ranges of experimental parameters over which the expression is known to be valid are given in Table 1-1.

A comparison of the calculated values to experimental data shows that the expression in Table 1-1 predicts the actual performance of the SMC within 9% over the range of conditions investigated.

1.1.2 Sabatier Reaction Model

Tests performed under Contract No. NAS2-11829 have shown that the efficiency for H₂ transmission is 100% under conditions that are readily accessible. For example, when the thickness of the cathode is 0.025 cm (0.010 in), the H₂ transmission efficiency is 100% for temperatures above 344 K (160 F), pressure differentials of at least 414 kN/m² (60 psid) and current densities of 45 mA/cm² (42 ASF) or less. Higher temperatures and/or larger pressure differentials permit the current density to be increased while still maintaining 100% H₂ transmission efficiency.

Under these conditions the flow of H₂ into the methanation reaction zone is controlled only by the current applied to the cell:

$$F_{H_2} = 3.109 \times 10^{-4} I \quad (1)$$

where:

$$\begin{aligned} F_{H_2} &= \text{Flow rate of H}_2 \text{ into methanation zone, moles H}_2/\text{min} \\ I &= \text{Applied current, A} \end{aligned}$$

As shown in Figure 1-2, the H₂ flows into the methanation zone of the IORS over the entire length of the zone. In the case of the tubular IORS geometry used in the Breadboard IORS, the H₂ flows into the volume containing the methanation catalyst over the entire surface area of that volume. This means that the composition of the gases in the methanation zone changes, not only because of the reaction of CO₂ and H₂, but also because of the way the H₂ is provided.

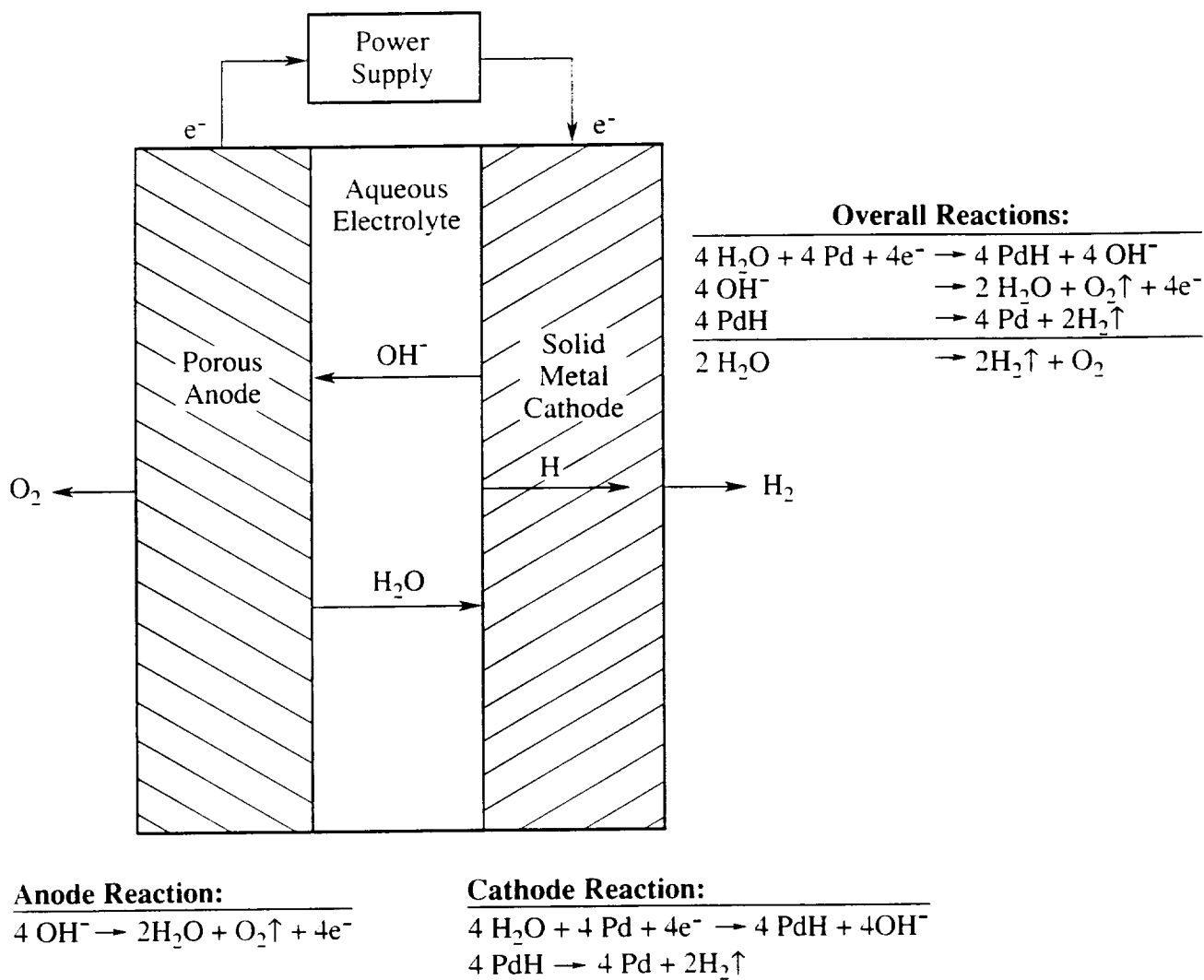


FIGURE 1-1 FUNCTIONAL SCHEMATIC AND REACTIONS FOR
SOLID METAL CATHODE CELL

TABLE 1-1 SOLID METAL CATHODE EMPIRICAL HYDROGEN
TRANSMISSION MODEL^(a)

$$t = a \exp(-E_0/RT) [P_{H_2}]^b [P_{O_2}]^c [CD]^d$$

where:

t = H_2 Transmission efficiency, %

a, b, c, d = Regression constants

a = 22,382 %

b = -0.987

c = 0.080

d = -0.474

E_0 = Regression activation energy constant, 2.610.5 cal/g-mole

R = Gas constant, 1.987 cal/g-mole K

T = Absolute temperature, K

P_{H_2} = Hydrogen chamber pressure, atm

P_{O_2} = Oxygen chamber pressure, atm

CD = Current density, mA/cm²

(a) Experimental parametric ranges:

Current density, mA/cm ²	: 45-90
Differential pressure, kN/m ²	: 1,034
Temperature, K	: 333-352
Hydrogen pressure, atm	: 0.951-0.968

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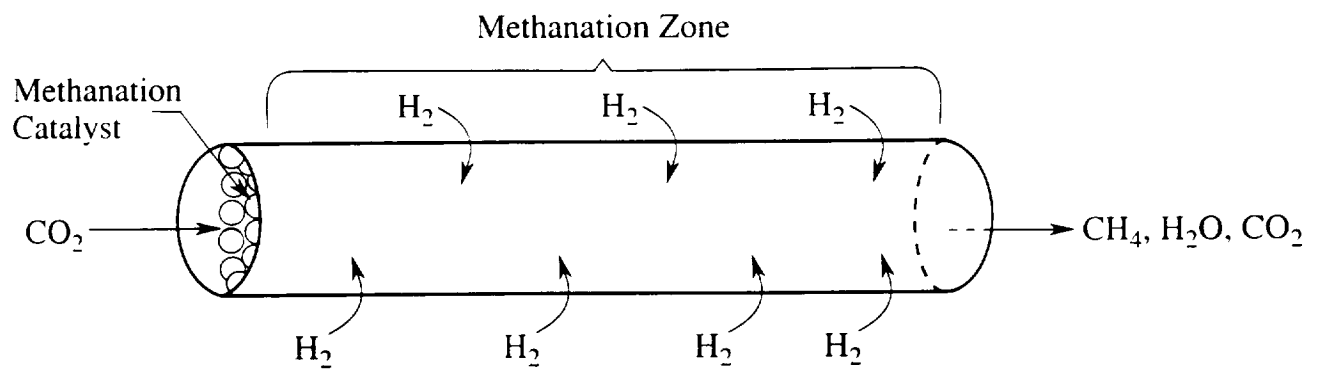
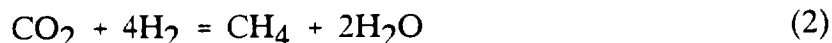


FIGURE 1-2 GAS FLOWS IN THE IORS METHANATION ZONE

The methanation reaction for CO₂ is:



The rate expression for this reaction has been reported to be^(a):

$$r_{\text{CO}_2} = A \exp(-E_A/RT) \left[P_{\text{CO}_2}^N P_{\text{H}_2}^{4N} - \frac{P_{\text{CH}_4}^N P_{\text{H}_2\text{O}}^{2N}}{K_{\text{eq}}^N} \right] \quad (3)$$

where:

- r_{CO_2} = Rate of conversion of CO₂ to CH₄, moles CO₂/cc catalyst-min
- A = Pre-exponential rate constant, moles/cc-min-atm^{5N}
- E_A = Activation energy, cal/mole
- N = Reaction order
- R = Universal gas constant, 1.987 cal/mole-K
- T = Temperature, K
- P_i = Partial pressure of gas, i, atm
- K_{eq} = Equilibrium constant for Equation (2), atm⁻²

The value of K_{eq} varies with temperature as shown below:

$$K_{\text{eq}} = \exp \left[\frac{1}{R} \left(\frac{56,000}{T^2} + \frac{34,633}{T} - 16.4 \ln T + 0.00557T \right) + 33.165 \right] \quad (4)$$

The moles of each species of gas present anywhere in the IORS methanation zone can be represented as follows:

$$\text{CO}_2 = (1-X) F \quad (5)$$

$$\text{H}_2 = C L^{-4} X F \quad (6)$$

$$\text{CH}_4 = X F \quad (7)$$

$$\text{H}_2\text{O} = 2 X F \quad (8)$$

(a) Verostko, C. E. and Forsythe, R. K., "A Study of the Sabatier-Methanation Reaction Kinetics," SAE Paper No. 740933, Presented at the Intersociety Conference on Environmental Systems, Seattle, WA; July 29 - August 1, 1974.

where:

- X = Fractional conversion of CO₂
- F = Feed rate of CO₂, moles/min
- L = Distance from beginning of methanation zone, cm
- C = Flux constant for H₂ transmission, moles H₂/min-cm

The parameter, C, equals the total moles of H₂ that transports into the methanation zone per minute, divided by the overall length of the methanation zone.

The total moles of gas in the methanation zone at any point, L, is given by Equation (9):

$$M = F + C L - 2 X F \quad (9)$$

where:

M = Total quantity of gas, moles

The mole fraction, Y, of each gas is therefore given by the following:

$$Y_{CO_2} = \frac{(1-X)F}{M} \quad (10)$$

$$Y_{H_2} = \frac{C L - 2 X F}{M} \quad (11)$$

$$Y_{CH_4} = \frac{X F}{M} \quad (12)$$

$$Y_{H_2O} = \frac{2 X F}{M} \quad (13)$$

Assuming ideal gas behavior, the partial pressure of each gas is equal to the mole fraction, multiplied by the total pressure in the IORS:

$$P_i = Y_i P_T \quad (14)$$

where:

- Y_i = Mole fraction of gas, i
- P_T = Total pressure in methanation zone, atm

Equation (4), with Equation (14) for each gas, can be substituted into Equation (3) to solve the rate expression for CO₂ conversion. However, before this can be accomplished, an additional step must be performed because the rate of CO₂ conversion will vary through the methanation zone since the concentration of H₂ will vary due to the transport process shown in Figure 1-2. In this situation the following relationship holds:

$$r_{\text{CO}_2} = F \frac{dX}{dV} \quad (15)$$

where:

V = Volume of catalyst in the IORS, cc

If we define a parameter, A_o, to equal the volume of catalyst per unit length of the methanation zone, then:

$$r_{\text{CO}_2} = F \frac{dX}{A_o dL} \quad (16)$$

Rearranging Equation (16) gives:

$$\frac{dX}{dL} = \frac{A_o}{F} r_{\text{CO}_2} \quad (17)$$

Inserting Equation (3) gives:

$$\frac{dX}{dL} = \frac{A_o}{F} A \exp(-E_A/RT) \left[P_{\text{CO}_2}^N P_{\text{H}_2}^{4N} - \frac{P_{\text{CH}_4}^N P_{\text{H}_2\text{O}}^{2N}}{K_{\text{eq}}^N} \right] \quad (18)$$

The partial pressures of the gases can be replaced by the expression given in Equation (14) using the mole fractions given in Equations (10) through (13). The result is Equation (19).

$$\frac{dX}{dL} = \frac{A_0}{F} A \exp(-E_A/RT) \left[\left(\frac{(1-X)FP_T}{M} \right)^N \left(\frac{(CL-4XF)P_T}{M} \right)^{4N} - \frac{1}{K_{eq}} \left(\frac{XFP_T}{M} \right)^N \left(\frac{2XFP_T}{M} \right)^{2N} \right] \quad (19)$$

This expression is difficult to integrate analytically. It can be solved using numerical analysis. Using a fourth order Runge-Kutta procedure, the basic algorithm is:

$$X_{N+1} = X_N + \frac{1}{6} (K_1 + 2K_2 + 2K_3 + K_4) \quad (20)$$

where:

$$\begin{aligned} K_1 &= h f(L_N, X_N) \\ K_2 &= h f(L_N + h/2, X_N + K_1/2) \\ K_3 &= h f(L_N + h/2, X_N + K_2/2) \\ K_4 &= h f(L_N + h, X_N + K_3) \\ h &= \text{Step size} \end{aligned}$$

This procedure can be used to solve Equation (19). Experimental parameters related to the Breadboard IORS are listed in Table 1-2.

1.2 Design and Fabrication of the Breadboard IORS Cell

The Breadboard IORS cell has been designed and fabrication has been started. The cell is shown schematically in Figure 1-3. The palladium/silver (Pd/Ag) cathode is tubular, and it has been catalyzed on the interior and exterior surfaces using Life Systems' proprietary procedure. The anode is Life Systems' porous electrolysis anode. The two electrodes are separated by zirconia cloth, having a thickness of 0.038 cm (0.015 in).

Two portions of the anode are located on each side of the cathode, and are compressed together by means of three titanium nuts and bolts. This arrangement was selected because it will achieve the lowest cell resistance possible with the Breadboard cell.

The electrodes will be immersed in potassium hydroxide (KOH) electrolyte, which will be contained by a stainless steel accumulator. A drain located in the bottom of the accumulator allows electrolyte to be added or removed without disassembly of the cell.

TABLE 1-2 VALUES OF PARAMETERS
USED FOR BREADBOARD IORS

1. Parameters for 20% ruthenium on alumina catalyst^(a):

$$A = 8.16 \text{ moles/cc-atm}^{5N}\text{-min}$$

$$E_A = 8,920.8 \text{ cal/mole}$$

$$N = 0.21$$

2. Parameters related to end-item IORS application:

$$\text{H}_2/\text{CO}_2 \text{ mole ratio} = 3.20$$

3. Parameters related to Breadboard IORS:

$$L_T = 36.51 \text{ cm (14.37 in)}$$

$$P_T = 2.04 \text{ atm (30 psia)}$$

$$V = 1.36 \text{ cc (0.0827 in}^3\text{)}^{(b)}$$

(a) Verostko, C.E. and Forsythe, R. K., "A Study of the Sabatier-Methanation Reaction Kinetics," SAE Paper No. 740933, Presented at the Intersociety Conference on Environmental Systems, Seattle, WA; July 29 - August 1, 1974.

(b) Assuming 33% void volume.

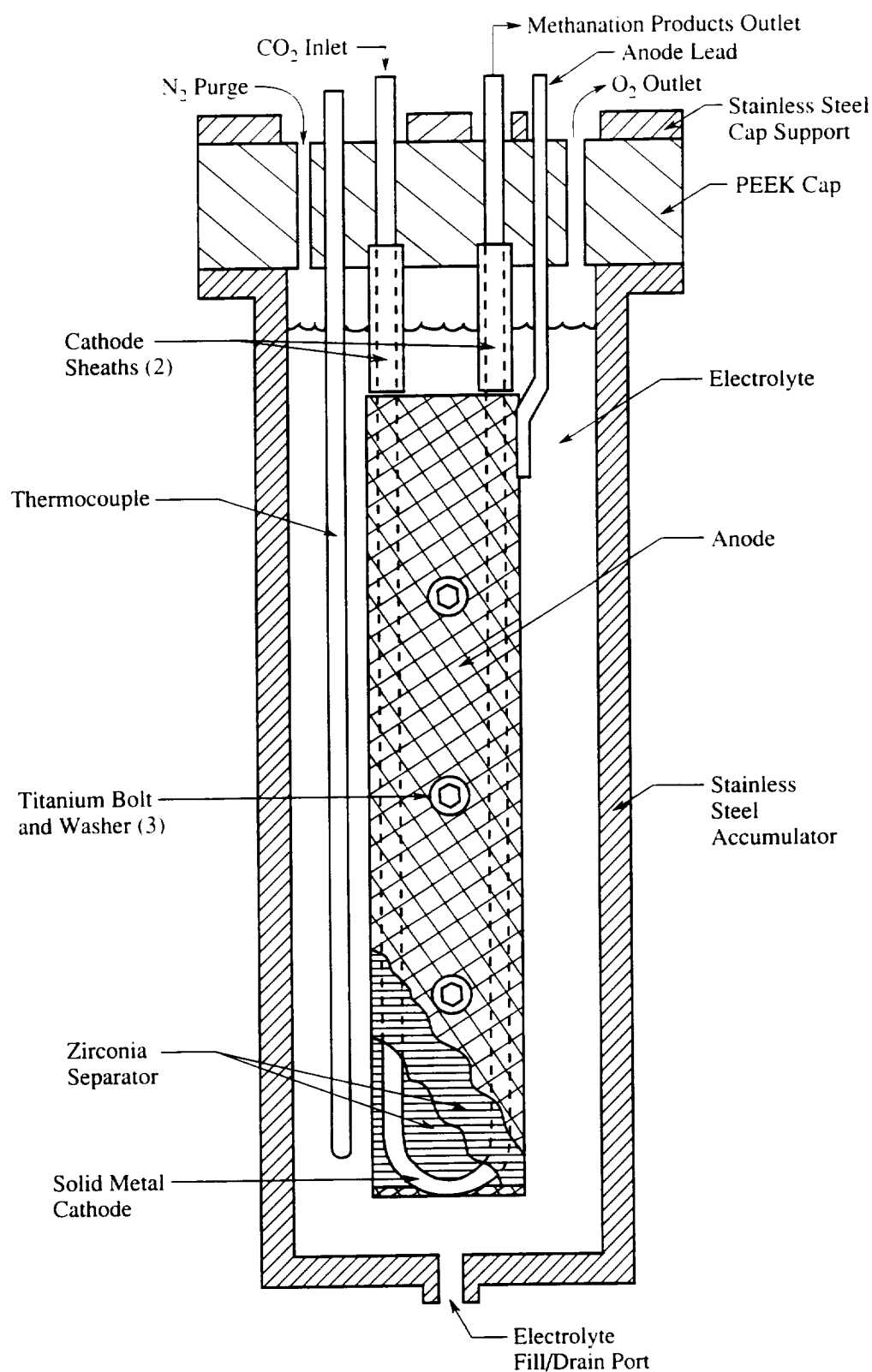


FIGURE 1-3 BREADBOARD IORS CELL

The top of the accumulator is sealed with a cap constructed of polyetheretherketone (PEEK), which is reinforced with 30% glass fibers for added strength at high temperature. The PEEK is further reinforced by a disk of stainless steel at the top. The PEEK cap provides electrical insulation for the electrodes which pass through it. Electrical contact to the electrodes will be made on the outside the cell. Because of the O-rings selected for sealing the accumulator and fittings, the maximum operating temperature of the Breadboard IORS cell is anticipated to be 505 K (450 F).

1.3 Design and Fabrication of Test Setup

The test setup to be used to demonstrate the feasibility of the IORS is shown schematically in Figure 1-4. Its legend is provided in Figure 1-5. The test setup has the capability of purging the O₂ and H₂ sides of the Breadboard IORS cell with nitrogen (N₂). Carbon dioxide will be provided from a cylinder, and if desired, H₂ can be provided also.

Flow meters will measure the flow rate of the reactants into the Breadboard IORS, and pressure gauges will be utilized to measure the pressure drop across the methanation catalyst, as well as the operating pressures on the O₂ and H₂ sides of the cell. Pressure regulators PR3 and PR4 allow the pressure within the O₂ and H₂ sides, respectively, of the Breadboard IORS cell to be adjusted.

A heating tape (H1) will be used to raise the temperature of the Breadboard IORS cell to its operating levels, while other heating tapes (H2 and H3) are used to prevent condensation in the gas lines, prior to the collection of liquid water in the drying tubes, D1-D4.

The gas dryers D1-D4 are arranged to allow water vapor to be collected and measured in the minimum period of time, and the traps, TR1 and TR2, are provided to prevent liquid water from entering the gas chromatograph (GC), when chromatographic analysis of the product gases is performed.

When desired, electrolyte from the Breadboard IORS cell can be drained into tank, TK1, even when the electrolyte is hot.

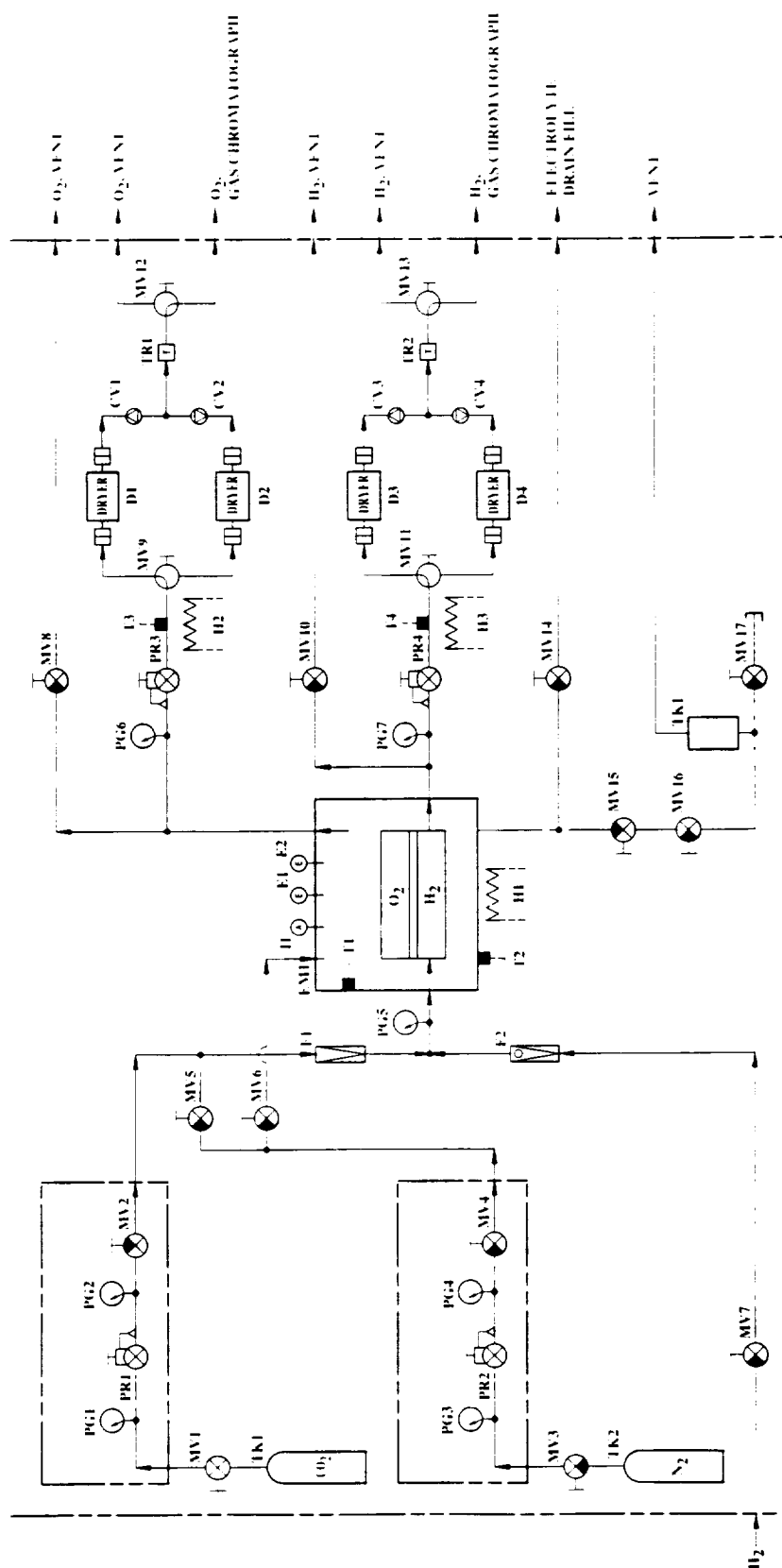


FIGURE 1-4 BREADBOARD IORS TEST SETUP MECHANICAL SCHEMATIC

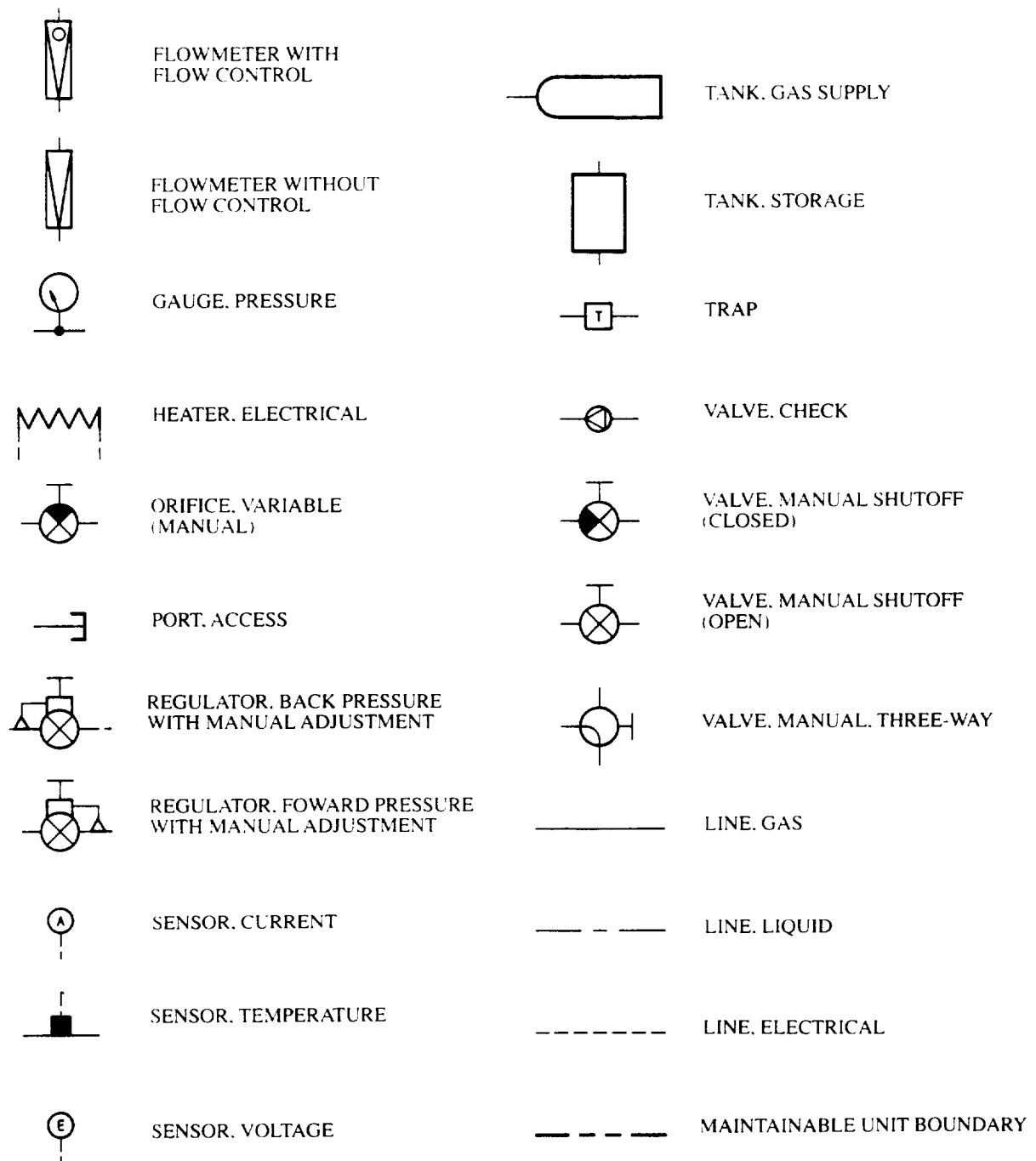


FIGURE 1-5 BREADBOARD IORS TEST SETUP
MECHANICAL SCHEMATIC (LEGEND)

2.0 PROBLEMS

No problems have been encountered which may impede performance or impact program schedule or cost.

3.0 WORK TO BE PERFORMED NEXT REPORTING PERIOD

Upon receipt of the PEEK, fabrication of the Breadboard IORS cell will be completed. The GC equipment will be set up and calibrated to permit measurement of O_2 -in- H_2 and H_2 -in- O_2 concentrations and the concentrations H_2 , CO_2 , O_2 , methane (CH_4) and carbon monoxide (CO) in the product gases exiting the methanation zone of the cell.

The cell will be integrated with the test setup and the Checkout and Shakedown tests will be completed. These tests will ensure that there are no leaks in the cell or test setup, and that accurate data can be obtained. Parametric tests will be started, including measurement of the temperature effect on the electrolysis and methanation reactions. A test of the effects of changes in gas composition on the methanation reaction, at the temperature identified as being the optimum, will also be started.

4.0 COST STATUS

The status of the program's cost is summarized below, as required by Attachment J-2 of Contract No. NAS8-39843.

- | | | |
|----|---|----------|
| 1. | Total cumulative costs as of 02/28/93: | \$22,059 |
| 2. | Estimated cost to complete contract: | \$27,941 |
| 3. | Estimated percentage of work completed: | 45% |

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 08 Mar 93	3. REPORT TYPE AND DATES COVERED Bimonthly Technical Progress Rpt. 08 Jan 93-08 Mar 93	
4. TITLE AND SUBTITLE Integrated Oxygen Recovery System Technical Progress Report No. 1			5. FUNDING NUMBERS NAS8-39843	
6. AUTHOR(S) Dr. M. Gene Lee and Dr. Ronald J. Davenport				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Life Systems, Inc. 24755 Highpoint Road Cleveland, OH 44122			8. PERFORMING ORGANIZATION REPORT NUMBER TR-1619-1-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration George C. Marshall Space Flight Center Marshall Space Flight Center, AL 35812			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE	
<p>13. ABSTRACT (Maximum 400 words)</p> <p>Life Systems has conceptualized an innovative Integrated Oxygen Recovery System (IORS) applicable to advanced mission air revitalization. The IORS provides the capability to electrochemically generate metabolic oxygen (O₂) and recover O₂ from the space habitat atmosphere via a carbon dioxide (CO₂) reduction process within a single assembly. To achieve this capability, the IORS utilizes a novel Solid Metal Cathode (SMC) water electrolysis unit that simultaneously serves as the Sabatier CO₂ reduction reactor. The IORS enables two major life support systems currently baselined in closed loop air revitalization systems to be combined into one smaller, less complex system. This concept reduces fluidic and electrical interface requirements and eliminates a hydrogen (H₂) interface.</p> <p>Life Systems is performing an evaluation of the IORS process directed at demonstrating performance and quantifying key physical characteristics including power, weight and volume. In this report, technical progress achieved during the first two months of the program is summarized.</p>				
14. SUBJECT TERMS Oxygen, carbon dioxide, reduction, hydrogen, electrochemical Solid Metal Cathode, air revitalization, methanation, Sabatier			15. NUMBER OF PAGES 21	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	